Ni-Ferrite-Based Thermochemical Cycle for Solar Hydrogen Production

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Abstract: Ni-Ferrite (NiFe₂O₄) was prepared as a basic metal oxide for a solar hydrogen production cycle consisting of a methane reduction step and a water-splitting step. All steps were performed at relatively low temperatures (below 1073 K). In the CH₄-reduction step, it was confirmed that CH₄ reduction of the prepared Ni-ferrite progressed through two reaction regions with an increase of reaction time. In one, CH₄ reacted with oxygen discharged from Ni-ferrite (region 1); in the other, the methane self-decomposition occurred (region 2). The water splitting step was performed using the reduced Ni-ferrite after the CH₄ reduction step in the two regions. In the water splitting step after the CH₄ reduction step (region 1), CO and CO₂ gas were not detected. The maximum H₂ production rate was about 3.3 mL/min g-metal-oxide at 10 min. The H₂ production rate in the water splitting step after the CH₄ reduction step (region 2) was about 3.3 mL/min g-metal-oxide at any reaction time. We confirmed from the XRD patterns that the phase of the prepared Ni-bearing ferrites was changed in each reaction step and that the phase after the water splitting step returned to the phase before the methane reduction step.

Keywords: water-splitting, hydrogen production, solar heat, Ni-ferrite, catalyst

Introduction

Hydrogen is an attractive fuel for future use because it is renewable as an energy resource and it is also flexible as an energy carrier. Specially, if hydrogen is used as a fuel, it does not release environmental pollutants such as carbon dioxide (CO₂) and sulfur dioxide (SO₂). Therefore, if human beings desire to obtain the ultimately clean H₂ as an energy carrier, water is its main source on earth. However, a very high temperature (above 4000 K) is required to obtain the H₂ directly from the water under 1 atm. To solve this problem, thermochemical water splitting cycles have been proposed for the hydrogen production from water at temperatures below 1100 K [1]. One of the most promising approaches for large-scale hydrogen production is to use heat energy from nuclear and solar sources [2-6]. On the other hand, the water splitting cycles mediated by metal oxides using the heat energy provided by concentrated solar radiation has been investigated.

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The water splitting method mediated by a metal oxide (Fe₂O₃/FeO) using the heat energy provided by concentrated solar radiation was investigated by Nakamura [7]. He proposed the following reactions:

\[ \text{Fe}_2\text{O}_4 \rightarrow 3\text{FeO} + \frac{1}{2}\text{O}_2 \]  
\[ \text{H}_2\text{O} + 3\text{FeO} \rightarrow \text{Fe}_3\text{O}_4 + \text{H}_2 \]

The thermal decomposition of Fe₂O₄ (magnetite) to wüstite (FeO) in reaction (1) proceeds endothermically in air at temperatures above 2300 K and 1 atm; it is called the solar reaction step. However, this proposed process has problems, such as the materials and process technologies required at the high temperature (a loss of the concentrated solar radiation) [8,9]. Reaction (2) is an exothermic reaction and the wüstite (FeO) is reoxidized to magnetite (Fe₂O₄) by water to produce hydrogen; it is called the water splitting step.

Tamura and coworkers [10] and Steinfeld and coworkers [11,12] proposed the combination of the decomposition of metal oxide with natural gas, such as CH₄, to decrease the process operation temperature, as shown in
the following reactions, which comprise the solar methane reforming process:

\[ \text{Fe}_2\text{O}_4 + \text{CH}_4 \rightarrow 3\text{FeO} + \text{CO} + 2\text{H}_2 \]  (3)
\[ \text{H}_2\text{O} + 3\text{FeO} \rightarrow \text{Fe}_2\text{O}_3 + \text{H}_2 \]  (4)

Here, CH\(_4\) is used for the activation of the metal oxide and the production of CO and H\(_2\), which are used for the synthetic gas. The operating temperature of thermal decomposition of metal oxide combined with CH\(_4\), as shown in Equation (3), is relatively low, which has merit for the two-step water splitting cycle, but CO\(_2\) formation is thermodynamically more favorable at a lower temperature during the CH\(_4\) reduction of metal oxide. The choice of metal oxide in reaction (3), which determines the high selectivity and reactivity for CO formation, is very important to avoid CO\(_2\) emission.

Several metal oxide redox pairs, such as ZnO/Zn\(_2\)O, TiO\(_2\) / TiO\(_2\) (with x < 2), MnO/Mn\(_2\)O\(_4\), CoO/Co\(_2\)O\(_4\), \(\text{Mg}_2\text{O}_4\), and \((\text{Fe}_{1-x}\text{M}_x)_2\text{O}_3/\text{Fe}_{1-x}\text{M}_{1-x}\text{O}_2\) (M = Mn, Mg, and Co) have been examined for application in multi-step water splitting cycles (more than two) [11-17]. These metal oxide redox pairs all provide problems, such as high operating temperatures, limits of the efficiency of the water splitting cycle, low hydrogen production yield, and the stability of the reduced phases in the water splitting. Kodama and coworkers [18] reported that Ni-ferrite was more reactive as an oxidant in the conversion of CH\(_4\) to CO and H\(_2\) than other thermostable metal oxides. They used a ZrO\(_2\) support for Ni-ferrite preparation and an experimental temperature of 1073 ~ 1173 K in a two-step processes. In their results, the undesired carbon deposited on the Ni-ferrite led to a decrease in the reactivity of the metal oxide.

In this study, Ni-ferrite (NiFe\(_2\)O\(_4\)) was prepared as a basic metal oxide and examined for the two-step water splitting cycles, consisting of the CH\(_4\) reduction and water splitting steps, at a relatively low temperature (below 1073 K). The characteristics of the prepared Ni-ferrite in each reaction were evaluated.

**Experimental**

**Synthesis of Ni-ferrites (NiFe\(_2\)O\(_4\))**

The Ni-ferrite was prepared as follows. Appropriate portions of ferric chloride (FeCl\(_3\)) and nickel chloride (NiCl\(_2\)) were dissolved separately in distilled water, and then mixed at 60°C. The molar ratio Ni/Fe\(_{\text{total}}\) in the starting solution was 0.5 to synthesize stoichiometric NiFe\(_2\)O\(_4\). 1 NaOH solution was added to the mixed solution of metal chlorides at 60°C, adjusting it to pH 10 for co-precipitation. The co-precipitate formed was aged for 10 h at room temperature, and then the precipitate was obtained by filtering and washing with distilled water and acetone. The products were dried at 100°C for 24 h. The obtained products were amorphous. They were sintered at 800, 1000, and 1200°C in a N\(_2\) gas atmosphere to crystallize as spinel-type ferrites. The flow rate of N\(_2\) gas was kept at 50 mL/min. The prepared Ni-ferrites formed at 800, 1000, and 1200°C were named MBF-1, MBF-2, and MBF-3, respectively. The prepared Ni-ferrites were crushed to 60-140-mesh sized particles.

The Ni-bearing oxides prepared at each temperature were identified by X-ray diffractometry (XRD) using CuK\(_{\alpha}\) radiation (Rigaku, RAD-rA diffractometer).

**Two-step Water Splitting Cycles Using Ni-bearing Ferrites**

Figure 1 shows an experimental apparatus used for the two-step water-splitting cycles.

The prepared Ni-ferrite (MBF-1, 5 g) was placed in a quartz tube reactor (o.d.: 50 mm; length: 360 mm) and inserted into an IR (Infrared Rays) furnace. The following reactions were examined for the Ni-ferrite:

\[(\text{NiFe}_2\text{O}_4) + 4 \text{CH}_4 \rightarrow \text{reduced Ni-ferrite} + 4 (\text{CO} + 2\text{H}_2) \]  (5)
\[\text{reduced Ni-ferrite} + y \text{H}_2\text{O} \rightarrow (\text{NiFe})_y\text{O}_y + y \text{H}_2 \]  (6)

Equation (5) is referred to as the CH\(_4\) reduction step of Ni-ferrite, and Equation (6) as the water splitting step.

The CH\(_4\) reduction step of Ni-ferrite was performed first. CH\(_4\) gas was introduced into the reactor at a flow rate of 50 mL/min. The reactor incorporating Ni-ferrite was heated to 700°C over about 1 min. After reaching 700°C, the temperature was kept constant. The CH\(_4\) gas was then substituted by Ar gas (50 mL/min, 2 h) to progress to the next step.

The water-splitting step was then performed. The reactor was heated to 650°C with a flow of the argon
carrier (50 mL/min). The steam, which produced by a steam generator at 250°C, was mixed with the argon gas. The flow rate of argon was maintained at 50 mL/min and the flow rate ratio of Ar: H2O was maintained at 1:1. The reduced metal-bearing ferrite reacted with H2O when passing the mixed Ar/H2O gas through the reactor.

To determine the total amounts of the products, the flow rates of the inert and outlet gases were measured using the bubble flow meter. The outlet gases in each step were analyzed by a gas chromatograph (GC) equipped with a TCD. To catch H2O to be sub-reactant, a cold trap was placed in the front of the GC.

The metal oxides, after examination at each step, were identified by XRD.

Results and Discussion

Synthesis of Ni-bearing Ferrites (NiFe2O4)

Figure 2 shows the XRD pattern of the Ni-bearing ferrite prepared at 800°C.

As shown in Figure 2, the Ni-bearing ferrites prepared at 800°C were crystallized as spinel-type ferrites and synthesized NiFe2O4. The Ni-bearing ferrites prepared at 1000 and 1200°C showed almost the same XRD patterns as that in Figure 2. It seems that sintering temperatures of 800 ~ 1200°C were suitable to obtain the desired NiFe2O4 in this study.

The median particle sizes of MBF-1, MBF-2, and MBF-3 analyzed by using a Particle Size Analyzer 22 (Fritsch Co.) were 20.63, 54.68, and 56.11 μm, respectively.

Two-step Water Splitting Cycles Using Ni-bearing Ferrites

CH4 Reduction Step

Figure 3 shows the relationship between the flow rates of each gas and the reaction time for the CH4 reduction step using MBF-1.

Upon an increase in the reaction time, the flow rate of CH4 gas decreased and that of the production gases, H2, CO, and CO2 increased until 20 min, before remaining constant until 50 min (Region 1). The flow rate of CH4 gas increased rapidly and that of H2 increased rapidly from 50 to 60 min, and then they remained almost constant after 60 min. The flow rates of CO and CO2 after 50 min decreased with increasing reaction time and they finally reached almost zero after 120 min (Region 2).

The results shown in Figure 3 can be explained as follows: In Region 1, CH4 gas actively reacted with the oxygen discharged from NiFe2O4 during the first 20 min and produced CO, CO2, and H2 gases, and then reaction rate remained constant until 50 min with the almost same production rates of the CO, CO2 and H2 gases. In Region 2, the CH4 gas began its self-decomposition after 50 min such that the hydrogen gas production increased significantly relative to that in Region 1, and then CH4 decomposition proceeded upon further increases of the reaction time such that the production rates of CO and CO2 decreased. Therefore, in this region, C (carbon) was largely deposited on the Ni-ferrite and H2O was also produced abundantly, as was confirmed from a few increased weights for and in the existence cold trap of H2O after the experiment.

Figure 4 shows the XRD pattern of Ni-ferrite after the CH4 reduction step in Region 2. We observe that Ni-ferrite after the CH4 reduction step was transformed to a Ni-Fealloy and carbon was deposited.

From those explanations and the data from Figure 3, the reaction equation for the CH4 reduction step in Region 2 is assumed to be:

$$\text{NiFe}_2\text{O}_4 + 4\text{CH}_4 \rightarrow \text{Ni-Fealloy} + 4\text{H}_2\text{O} + 4\text{H}_2 + 4\text{C} \text{ (deposited)}$$

(7)

From these results, suitable reaction times to avoid the deposit of carbon on the Ni-ferrite during the CH4 reduction step are within 45 min.
Figure 4. XRD pattern of Ni-ferrite after the CH₄ reduction step in Region 2.

Water Splitting Step After CH₄ Reduction Step in Regions 1 and 2

Figure 5 shows the relationship between the flow rate of hydrogen gas and the reaction time for the water splitting step after the CH₄ reduction step in Regions 1 and 2 using MBF-1.

As shown in Figure 5-(a), the flow rate of H₂ increased as the reaction time increased, and reached a maximum value at 10 min, and then it decreased. Gases such as CO and CO₂, which we expected to be sub-reactants, were not detected. It seems that the decreasing flow rate of H₂ was due to reaching the saturation state of the Ni-Fealloy that had reacted with the oxygen that had separated from water.

The maximum H₂ production rate after the CH₄ reduction step in Region 1 was about 3.3 mL/min g-metal oxide at 10 min.

As shown in Figure 5-(b), with an increase in the reaction time, the flow rates of the production gases H₂ and CO increased until 40 min, and then they slowly decreased. The flow rate of CO₂ increased until 60 min and then remained almost constant upon increasing the reaction time. It seems that the produced CO and CO₂ gas arose from the reaction of the deposited carbon formed after the CH₄ reduction step in Region 2 and the supplying steam.

The H₂ production rate after the CH₄ reduction step in Region 2 was about 3.3 mL/min g-metal-oxide at any reaction time.

It is expected from these results that the water splitting step after the CH₄ reduction step in Region 1 is preferable compared with that in Region 2 from the viewpoint of the non-release of the CO and CO₂ gases.

Figure 6 shows the XRD patterns obtained after the water-splitting step.

Figure 5. The relationship between the flow rates of each gas and the reaction time for the water splitting step after the CH₄ reduction step in the two reaction regions using MBF-1.

Figure 6. XRD patterns obtained after the water splitting step using the metal examined from the CH₄ reduction step in the two reaction regions.
We observe from Figure 6-(a) that the Ni-Fe alloy was transformed in to (NiFe)O₃. From these XRD data and the data from Figure 5-(a), the reaction equation for the water splitting step after the CH₄ reduction step (Region 1) is assumed to be:

\[
\text{Ni-Fealloy} + 4\text{H}_2\text{O} \rightarrow (\text{NiFe})_3\text{O}_4 + 4\text{H}_2 
\]

(8)

We also observed from Figure 6-(b) that the metal Ni-Fe alloy was transformed in to (NiFe)O₃ and Ni-Fe alloy. From these XRD data and the data of Figure 5-(b), the reaction equation for the water splitting step after the CH₄ reduction step (Region 2) is assumed to be:

\[
\text{Ni-Fealloy} + 9\text{H}_2\text{O} + 3\text{C} \rightarrow (\text{Ni-Fealloy} + \text{NiFe}_2\text{O}_4) + 2\text{CO}_2 + \text{CO} + 9\text{H}_2 
\]

(9)

It is expected from those results that the phase of the prepared Ni-bearing ferrites is changed in each reaction step and that the phase after the water splitting step returns to the phase before the CH₄ reduction step.

From these results, we conclude that the prepared Ni-ferrite can be used in the water splitting cycles using the heat energy provided by concentrated solar radiation with its phase returning, low operation temperature, and relatively high hydrogen production rate.

For further study, it is necessary to clarify the stability of the prepared Ni-ferrites by repeating the experiments of the two-step water splitting cycles for a longer lifetime and to evaluate the thermal efficiency.

**Conclusions**

1. Ni-Bearing ferrites (NiFe₂O₄) were prepared as a basic metal oxide for the two-step water splitting cycles consisting of a CH₄ reduction step and a water splitting step using solar heat.
2. All steps were carried out at relatively low temperature (below 1073 K). In the CH₄ reduction step, we confirmed that the CH₄ reduction of the prepared Ni-ferrite progressed through two reaction regions with an increase of reaction time. One is that CH₄ reacted with oxygen discharged from Ni-ferrite; the other is that the methane under went a self-decomposition reaction.
3. The water splitting step was carried out after the CH₄ reduction step in the two regions. From our results, performing the water splitting step after the CH₄ reduction step in Region 1 is preferable to that in Region 2 from the viewpoint of the non-release of CO and CO₂. The maximum H₂ production rate of the metal after the CH₄ reduction step in Region 1 was about 3.3 mL/min g-metal-oxide at 10 min. The H₂ production rate after the CH₄ reduction step in Region 2 was about 3.3 mL/ min g-metal-oxide at any reaction time.
4. We confirmed from XRD analysis that the phase of the prepared Ni-ferrite changed in each reaction step and that the phase after the water splitting step returned to the phase that existed before the CH₄ reduction step.

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**References**